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XXXIX. *Some Observations on ancient Inks, with the Proposal of a new Method of recovering the Legibility of decayed Writings.* By Charles Blagden, M. D. Sec. R. S. and F. A. S.

Read June 28, 1787.

**I**N a conversation some time ago with my friend THOMAS ASTLE, Esq. F. R. S. and A. S. relative to the legibility of ancient MSS. a question arose, whether the inks in use eight or ten centuries ago, and which are often found to have preserved their colour remarkably well, were made of different materials from those employed in later times, of which many are already become so pale as scarcely to be read. With a view to the decision of this question, Mr. ASTLE obligingly furnished me with several MSS. on parchment and vellum, from the ninth to the fifteenth centuries inclusively; some of which were still very black, and others of different shades of colour, from a deep yellowish brown to a very pale yellow, in some parts so faint as to be scarcely visible. On all of these I made experiments with the chemical re-agents which appeared to me best adapted to the purpose; namely, alkalies both simple and phlogificated, the mineral acids, and infusion of galls.

It would be tedious and superfluous to enter into a detail of the particular experiments; as all of them, one instance only excepted, agreed in the general result, to shew, that the ink employed anciently, as far as the above-mentioned

MSS.

MSS. extended, was of the same nature as the present: for the letters turned of a reddish or yellowish brown with alkalies, became pale, and were at length obliterated, with the dilute mineral acids, and the drop of acid liquor which had extracted a letter, changed to a deep blue or green on the addition of a drop of phlogisticated alkali; moreover, the letters acquired a deeper tinge with the infusion of galls, in some cases more, in others less. Hence it is evident, that one of the ingredients was iron, which there is no reason to doubt was joined with the vitriolic acid; and the colour of the more perfect MSS. which in some was a deep black, and in others a purplish black, together with the restitution of that colour, in those which had lost it, by the infusion of galls, sufficiently proved that another of the ingredients was astringent matter, which from history appears to have been that of galls. No trace of a black pigment of any sort was discovered, the drop of acid, which had completely extracted a letter, appearing of an uniform pale ferrugineous colour, without an atom of black powder, or other extraneous matter, floating in it.

As to the greater durability of the more ancient inks, it seemed, from what occurred to me in these experiments, to depend very much on a better preparation of the material upon which the writing was made, namely, the parchment or vellum; the blackest letters being generally those which had sunk into it the deepest. Some degree of effervescence was commonly to be perceived when the acids came in contact with the surface of these old vellums. I was led, however, to suspect, that the ancient inks contained a rather less proportion of iron than the more modern; for in general the tinge of colour, produced by the phlogisticated alkali in the acid laid upon them, seemed less deep; which, however, might depend in part upon the  
length

length of time they had been kept: and perhaps more gum was used in them, or possibly they were washed over with some kind of varnish, though not such as gave any gloss.

One of the specimens sent me by Mr. ASTLE proved very different from the rest. It was said to be a MS. of the fifteenth century; and the letters were those of a full engrossing hand, angular, without any *fine* strokes, broad, and very black. On this none of the above-mentioned re-agents produced any considerable effect; most of them rather seemed to make the letters blacker, probably by cleaning the surface; and the acids, after having been rubbed strongly upon the letters, did not strike any deeper ringe with the phlogisticated alkali. Nothing had a sensible effect toward obliterating these letters but what took off part of the surface of the vellum; when small rolls, as of a dirty matter, were to be perceived. It is therefore unquestionable, that no iron was used in this ink; and from its resistance to the chemical solvents, as well as a certain clotted appearance in the letters when examined closely, and in some places a slight degree of gloss, I have little doubt but they were formed with a composition of a black footy or carbonaceous powder and oil, probably something like our present Printer's ink, and am not without suspicion that they were actually printed\*.

Whilst I was considering of the experiments to be made, in order to ascertain the composition of ancient inks, it occurred to me, that perhaps one of the best methods of restoring legibility to decayed writing might be, to join phlogisticated alkali with the remaining calx of iron; because, as the quantity of pre-

\* A subsequent examination of a larger portion of this supposed MS. has shewn, that it is really part of a very ancient printed book.

precipitate formed by these two substances very much exceeds that of the iron alone, the bulk of colouring matter would thereby be greatly augmented. M. BERGMAN was of opinion, that the blue precipitate contains only between a fifth and a sixth part of its weight of iron; and though subsequent experiments \* tend to shew that, in some cases at least, the proportion of iron is much greater, yet upon the whole it is certainly true, that if the iron left by the stroke of a pen were joined to the colouring matter of phlogisticated alkali, the quantity of Prussian blue thence resulting would be much greater than the quantity of black matter originally contained in the ink deposited by the pen; though perhaps the body of colour might not be equally augmented. To bring this idea to the test, I made a few experiments as follows.

The phlogisticated alkali was rubbed upon the bare writing, in different quantities; but in general with little effect. In a few instances, however, it gave a bluish tinge to the letters, and increased their intensity, probably where something of an acid nature had contributed to the diminution of their colour.

Reflecting that when the phlogisticated alkali forms its blue precipitate with iron, the metal is usually first dissolved in an acid, I was next induced to try the effect of adding a dilute mineral acid to writing, besides the alkali. This answered fully to my expectations; the letters changing very speedily to a deep blue colour, of great beauty and intensity. It seems of little consequence as to the strength of colour obtained, whether the writing be first wetted with the acid, and then the phlogisticated alkali be touched upon it, or whether the process be inverted, beginning with the alkali; but on another account, I think, the

\* CRELL *Beyträge*, B. I. ft. 1. p. 42, &c.

latter way preferable. For the principal inconvenience which occurs in the proposed method of restoring MSS. is, that the colour frequently spreads, and so much blots the parchment, as to detract greatly from the legibility; now this appears to happen in a less degree when the alkali is put on first, and the dilute acid is added upon it. The method I have hitherto found to answer best has been, to spread the alkali thin with a feather over the traces of the letters, and then to touch it gently, as nearly upon or over the letters as can be done, with the diluted acid, by means of a feather, or a bit of stick cut to a blunt point. Though the alkali has occasioned no sensible change of colour, yet the moment that the acid comes upon it, every trace of a letter turns at once to a fine blue\*, which soon acquires its full intensity, and is beyond comparison stronger than the colour of the original trace had been. If now the corner of a bit of blotting paper be carefully and dexterously applied near the letters, so as to suck up the superfluous liquor, the staining of the parchment may be in great measure avoided: for it is this superfluous liquor, which, absorbing part of the colouring matter from the letters, becomes a dye to whatever it touches. Care must be taken not

\* The *phlogificated alkali* (which is to be considered simply as a name) appears to consist of a peculiar acid, in the present extensive acceptation of that term, joined to the alkali. Now the theory of the above-mentioned process I take to be, that the mineral acid, by its stronger attraction for the alkali, dislodges the colouring (Prussian) acid, which then immediately seizes on the calx of iron, and converts it into Prussian blue, without moving it from its place. But if the mineral acid be put upon the writing first, the calx of iron is partly dissolved and diffused by that liquor before the Prussian acid combines with it; whence the edges of the letters are rendered more indistinct, and the parchment is more

to bring the blotting paper in contact with the letters, because the colouring matter is soft whilst wet, and may easily be rubbed off.

The acid I have chiefly employed has been the marine; but both the vitriolic and nitrous succeed very well. They should undoubtedly be so far diluted as not to be in danger of corroding the parchment, after which the degree of strength does not seem to be a matter of much nicety.

The method now commonly practised to restore old writings, is by wetting them with an infusion of galls in white wine \*. This certainly has a great effect; but it is subject, in some degree, to the same inconvenience as the phlogisticated alkali, of staining the substance on which the writing was made. Perhaps if, instead of galls themselves, the peculiar acid or other matter which strikes the black with iron were separated from the simple astringent matter, for which purpose two different processes are given by PIEPENBRING † and by SCHEELÉ ‡, this inconvenience might be avoided. It is not improbable likewise, that a phlogisticated alkali might be prepared, better suited to this object than the common; as by rendering it as free as possible from iron, diluting it to a certain degree, or substituting the volatile alkali for the fixed. Experiment would most likely point out many other means of improving the process described above; but in its present state I

\* See a complicated process for the preparation of such a liquor in CANEPARIUS, *De Atramentis*, p. 277.

† CRELL. *Annal.* 1786, B. I. p. 51.

‡ Kongl. Vetensk. Acad. *Nya Handlingar*, tom. VII. p. 30. See also M. DE MORVEAU's account of this substance in the *Encyclopédie par ordre des matières*.

hope it may be of some use, as it not only brings out a prodigious body of colour upon letters which were before so pale as to be almost invifible, but has the further advantages over the infufion of galls, that it produces its effect immediately, and can be confined to thofe letters only for which fuch affiftance is wanted.

